

## Microstructures and Properties of Sintered Cu-MoS<sub>2</sub>/Cu Functional Gradient Materials

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**Abstract.** The Cu-MoS<sub>2</sub>/Cu functional gradient materials were prepared by powder metallurgy method. The effects of MoS<sub>2</sub> content on the microstructure, phase composition and wear performance were analyzed comprehensively. Solid-solid phase reaction occurred between MoS<sub>2</sub> and Cu in the sintering process. The products of such reaction are copper-molybdenum sulfur compounds, copper sulfide, and Mo complex. They are distributed uniformly in the grain boundary of the matrix. The transition layers existed in the Cu-MoS<sub>2</sub>/Cu gradient materials. With the increasing of MoS<sub>2</sub> content, the amount of solid-solid phase reaction products also increased, with little decreasing of the density, electrical conductivity and tensile strength of the materials. While the hardness and the thickness of the solid lubrication film drastically increased. Especially, when the content of MoS<sub>2</sub> was 3%, the electrical conductivity and the mechanical properties showed a better balance between themselves. Besides, the wear performance of the composite materials was the best.

### Introduction

The lubricating film, as a result of the transformation of lubricating medium in the solid self-lubricating composites to the friction interface of the friction pair in the working process, can exhibit the self-lubricating effect. Metal matrix self-lubricating composite material with excellent mechanical properties and tribological properties. They are used in atmosphere, electrical, chemical, high temperature, vacuum and other special conditions [1-5]. The development of space technology, composite materials with good physical and mechanical properties has become more inevitable. Graphite (G) and molybdenum disulfide (MoS<sub>2</sub>) in the copper matrix self-lubricating composite materials were common lubrication components. G and MoS<sub>2</sub> with hexagonal layered structure can exhibit excellent solid self-lubrication. Especially, MoS<sub>2</sub> is a better choice because the lubrication of G could fail in the vacuum. While MoS<sub>2</sub> shows a small friction coefficient, good thermal stability, high yield strength, excellent resistance to radiation and other excellent performance in the vacuum. Therefore, MoS<sub>2</sub> could be used widely with the development of modern machinery and aviation industry. MoS<sub>2</sub> as solid lubrication component is rarely used in the copper matrix composite materials [6,7].

During the conventional casting process, the local segregation caused by the flotation of particles is very serious. The flotation of MoS<sub>2</sub> particles is caused by the physical differences between copper alloy and MoS<sub>2</sub>. Although the semi-solid casting can eliminate segregation, its application is limited because of the narrow semi-solid casting temperature control range, higher requirements on equipments, complex technologies, low production efficiency and high production cost. MoS<sub>2</sub>/Cu self-lubricating composite materials produced by the Powder Metallurgy (P/M) methods have excellent performance. Because of P/M methods can change the component proportions over a wide range to adjust the comprehensive performance of materials. Moreover, MoS<sub>2</sub>/Cu self-lubricating composite materials have good antifriction, wear resistance due to MoS<sub>2</sub> and the dispersed phase caused by the solid-solid phase reaction between MoS<sub>2</sub> and Cu in the process of sintering [8,9]. The

functional gradient materials with copper and MoS<sub>2</sub>/Cu composites, with good electrical conductivity and excellent abrasion resistance, have a broad prospect in the field of space technology. The wear resistance tests of MoS<sub>2</sub>/Cu functional gradient materials produced by P/M were carried out at the room temperature and high temperature in vacuum. The effects of MoS<sub>2</sub> content on the microstructure, phase composition and wear performance were analyzed in this paper. It could provide the theory basis for the application of copper base functional gradient materials.

### Experimental Procedure

Copper powders (99.50% purity, <30 $\mu$ m) and MoS<sub>2</sub> powders (99.02% purity, <27 $\mu$ m) were used as raw materials. MoS<sub>2</sub>/Cu composite powders were mixed according to the quality of MoS<sub>2</sub> are 2, 3, 4 and 6%. Powders were mixed for 40 h by Y type mixer. 300 g of pure copper powder were putted into the bottom of the rubber mold (diameter was  $\Phi$ 45 mm), and then 300 g of MoS<sub>2</sub>/Cu composite powder was put on the pure copper powder. The powders was consolidated by cold isostatic pressing at 260 MPa for 30 min. Cold-press billets were first sintered up to 300 °C for 30 min, and then sintered protect by argon gas at 800 °C for 2 h.

The electrical conductivity, hardness, density and mechanical properties of Cu-MoS<sub>2</sub>/Cu composites were measured by D60K digital metal conductivity meter, MH-3 micro-hardness tester, Archimedes method, SHIMADZU AG-1250KN universal tensile testing machine, respectively. The wear performance of Cu-MoS<sub>2</sub>/Cu composites was tested by MMU-5GA vacuum high temperature friction and wear tester. The sliding velocity was 1600 r/min, the load was 100 N, and the test temperature is room temperature or 300°C under vacuum, and the friction pair was ordinary carbon steel. The samples were weighed with alcohol ultrasonic cleaning before and after wear test to calculate the weight loss. The microstructures and wear morphologies were observed by scanning electron microscope (JSM-5610LV). The phase of the material was analyzed by X ray diffraction analyzer (D/rmX-2400). The microstructure of test materials was analyzed by transmission electron microscopy (JSM2100).

### Results and Discussion

Fig. 1 shows transition layers in Cu-MoS<sub>2</sub>/Cu functional materials. The microstructure of the test materials had obvious transition zone, the left turned to be pure copper and the right to be MoS<sub>2</sub>/Cu composite materials. Copper matrix continually distributed from left to right and connected closely at the interface. Transition layers have a certain continuous thickness. It indicated that the diffusion took place between the copper and MoS<sub>2</sub> during the sintering process. The precipitated second phases were uniform distributed in the wear-resisting side. Test materials are compact, but there are tiny pores at the boundary of composite materials. With the increase of MoS<sub>2</sub> content, enhancement phase increased gradually due to the more and more reaction between copper and MoS<sub>2</sub>. The tiny particles aggregation distribution along with the matrix grain boundary and then formed to bulk. At the same time, the tiny holes increased along the borders of the second phases.

Fig. 2 shows the microstructure of wear-resisting side (MoS<sub>2</sub>/Cu). There are three phases in the MoS<sub>2</sub>/Cu composites: homogeneous continuous dark grey matrix phase, gray phase and dispersion distribution gray granular phase. According to the EDS result, the grey phases are complex copper-molybdenum sulfur compounds and they are distributed along the grain boundary. The diffuse distribution bright white particles are free stated molybdenum and it's dispersed in matrix grain and also the grain boundary. A small amount of tiny pore and holes exist in the boundary of grain of composite materials. XRD patterns of composite materials indicated that molybdenum and Cu<sub>1.84</sub>Mo<sub>6</sub>S<sub>8</sub> has obvious diffraction peaks, which is consistent with the results of EDS.

TEM images of MoS<sub>2</sub>/Cu composites contains 3% MoS<sub>2</sub> were shown in Fig. 3. It indicates that MoS<sub>2</sub> distributed in the matrix grain boundary, Fig. 3(a, b, e), accompanied by the precipitate of Mo nanocrystals, Fig. 3(b). The complex copper-molybdenum sulfur compounds (Cu<sub>1.84</sub>Mo<sub>6</sub>S<sub>8</sub>, Cu<sub>5.4</sub>Mo<sub>18</sub>S<sub>24</sub>) separated out the interface between the matrix and MoS<sub>2</sub> in the form of nanocrystals, Fig. 3(e,f). MoS<sub>2</sub> is distributed in the grain interior and the grain boundary of the

matrix, Fig. 3(d). The solid-solid phase reaction occurred between MoS<sub>2</sub> and Cu in the sintering process. The reaction products are Cu<sub>1.84</sub>Mo<sub>6</sub>S<sub>8</sub>, Cu<sub>5.4</sub>Mo<sub>18</sub>S<sub>24</sub>, Mo and Cu<sub>2</sub>S. Cu<sub>2</sub>S compounds with layered structure which is similar to that of the MoS<sub>2</sub>, can replace of MoS<sub>2</sub> as self-lubricating phase. The hard phase elemental Mo can improve the wear resistance of the test materials.

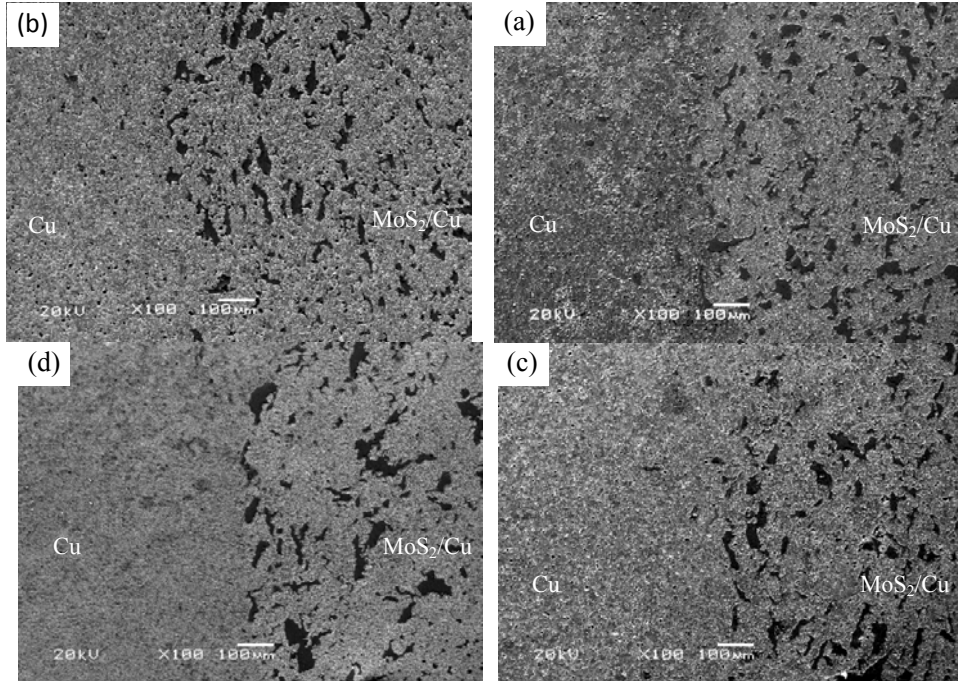


Fig. 1 Microstructures of composites with different MoS<sub>2</sub> contents (a)2%; (b)3%; (c)4%; (d)6%

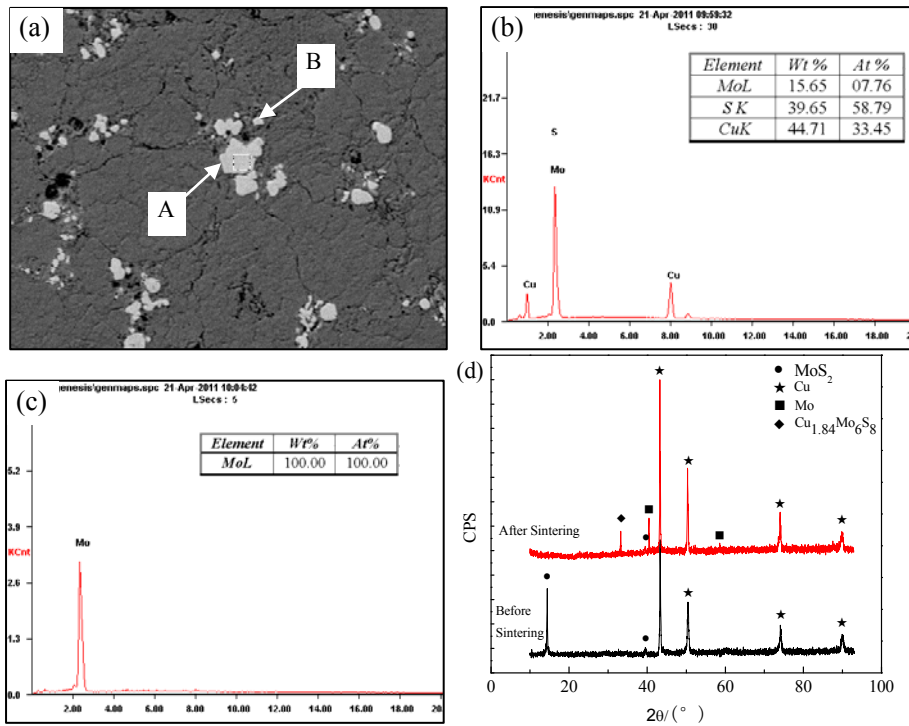


Fig.2 Microstructure analysis of composites with 3% MoS<sub>2</sub>: (a) SEM images; (b and c) EDS at the point of A and B; (d) XRD data

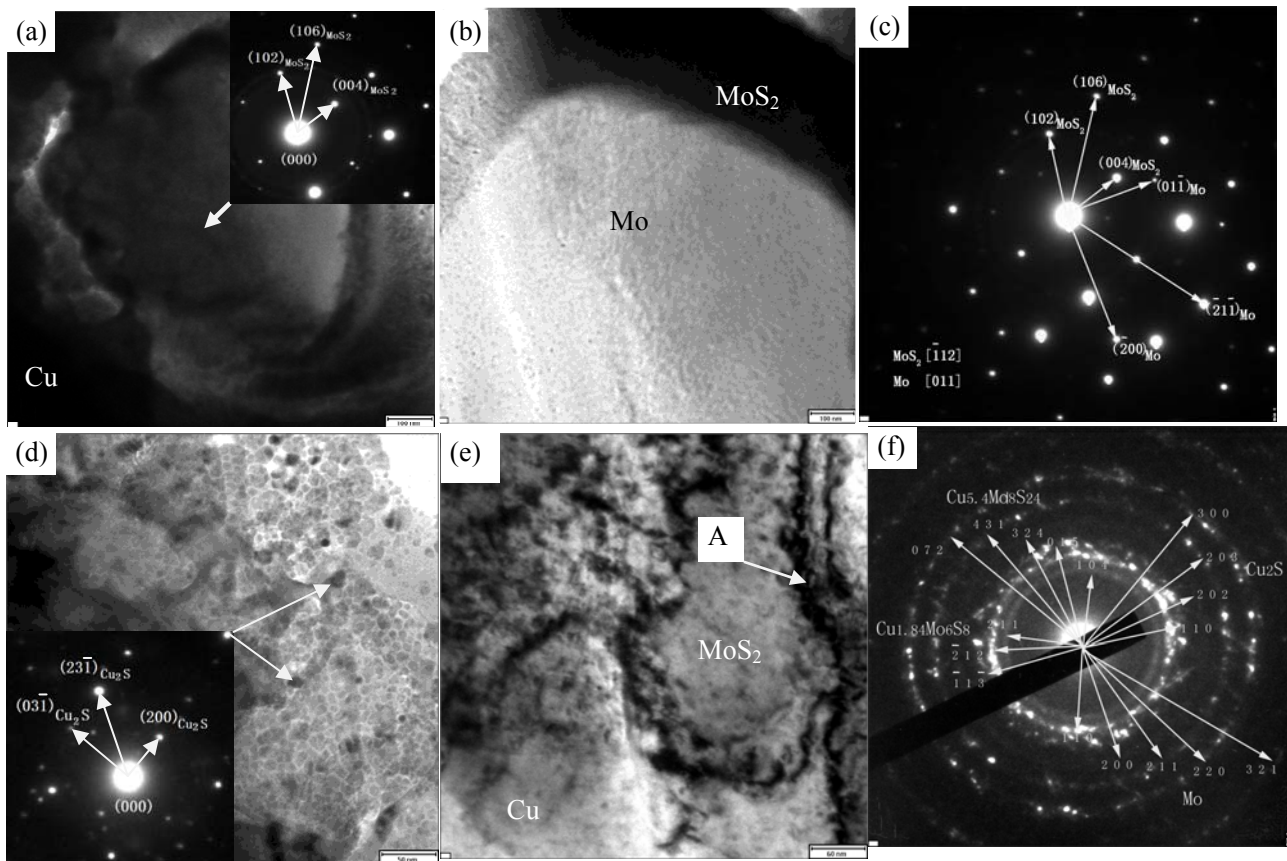


Fig.3 TEM images and selected area electron diffraction patterns of composites with 3% MoS<sub>2</sub>: (a, b, c and d) morphology and its diffraction pattern of Cu Mo, MoS<sub>2</sub> and Cu<sub>2</sub>S, respectively; (e) the precipitation phases and interface; (f) TEM diffraction at the point A in Fig. (e)

Fig.4 showed the relationship between the hardness, electric conductivity and MoS<sub>2</sub> content. With the increase of MoS<sub>2</sub>, the hardness increased while the electric conductivity decreased because of the soft and low hardness of copper metal. Due to the addition of reinforced phase, the hardness of composites increased. The reaction product Mo was a kind of hard phases, increase the dislocation density in the matrix and produce a large stress field, so it can strengthen the matrix. In the sintering process, MoS<sub>2</sub> reacted with copper matrix gradually and sintering production increased, which makes the metallic phase reduce while non-metallic phase increase, so the hardness of composite increased, but the electric conductivity reduced. The hardness and the electric conductivity have a better cooperation when the content of MoS<sub>2</sub> is 3%.

Fig. 5 shows that the density and relative density of testing materials. with the increase amount of MoS<sub>2</sub>, the density of composite reduced. Because the density of MoS<sub>2</sub> is much lower than the density of copper, meanwhile the density of the complex compounds that generated after sintering process is lower than fine copper. At the same time, the generation of sintering necks has a great connection with the diffusion of atoms in the sintering process. With the increase of MoS<sub>2</sub>, the effect of hindering the diffusion of atoms increased, so the porosity increase and the density reduce. In general, the relative density rises gradually and can reach above 98%. The tensile strength of function material with the content of MoS<sub>2</sub> is 2, 3, 4 and 6% were 146.7, 138, 117 and 101.4 MPa. With the increase of MoS<sub>2</sub>, the tensile strength reduced. The main reason is that the reaction products mainly distribute along the matrix grain boundary.

The weight loss of test material at room temperature and 300°C condition is shown in Fig.6. With the increase of the content of MoS<sub>2</sub>, the weight loss of test materials reduced and wears resistance increased. The weight loss of test material at room temperature was larger than that of at 300°C. With the increase of MoS<sub>2</sub> content, the difference of weight loss between 300°C and room temperature is reduced.

The wear morphology of test material was shown in Fig.7. To the composites without MoS<sub>2</sub>, it is not easy to form protective lubricant film. The wear surface is rough and weight loss is the largest. There are furrow due to plastic deformation and serious peeling wear (Fig.7a). With the of increase content of MoS<sub>2</sub>, the wear surface was more and more smooth (Fig.7 b, c). The continuous lubricating film caused by the transformation of MoS<sub>2</sub> and Cu<sub>2</sub>S in the MoS<sub>2</sub>/Cu composites, can effectively protect the friction pair [10].

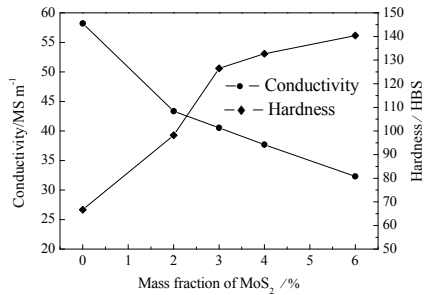


Fig.4 The changes of electrical conductivity and hardness with the mass fraction of MoS<sub>2</sub>

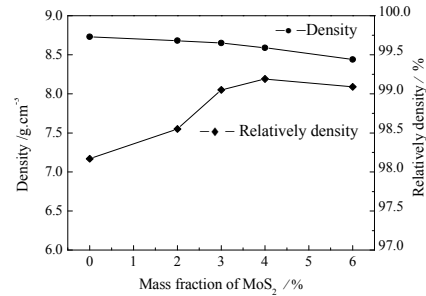


Fig.5 The change of the relative density with the mass fraction of MoS<sub>2</sub>

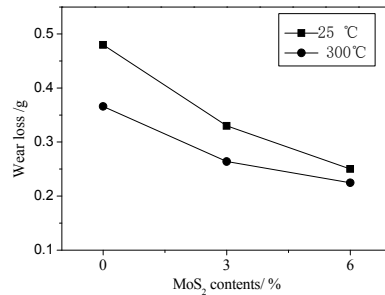


Fig.6 Wear loss of experiment material at room temperature and 300°C

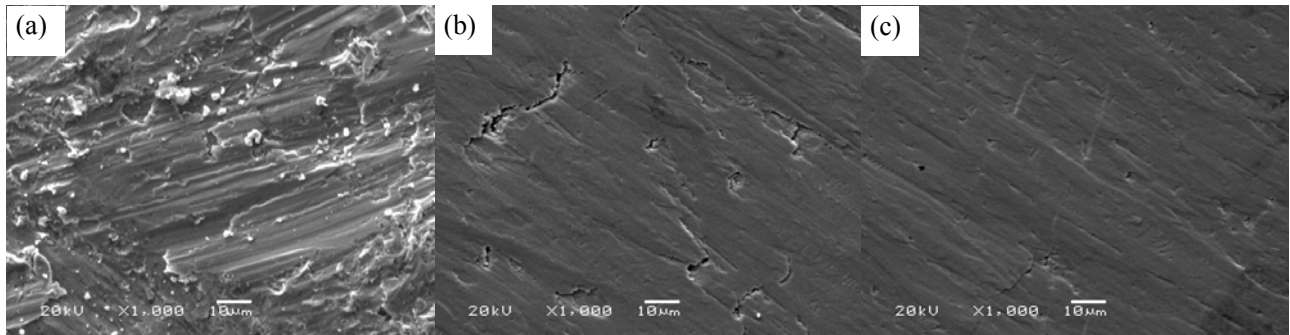


Fig.7 Wear morphology of composites with different contents of MoS<sub>2</sub> at room temperature: (a)0; (b)3%; (b) 6%

## Conclusions

(1) Solid-solid phase reaction occurred between MoS<sub>2</sub> and Cu in the sintering process. The products of such reaction are complex copper-molybdenum sulfur compounds, copper sulfide and Mo which distributed in the matrix grain boundary. The continuous transition layers can be observed.

(2) With the increase of MoS<sub>2</sub> content, the amount of solid-solid phase reaction products increased. The density, electrical conductivity and tensile strength of the materials decreased, while the hardness and the thickness of the solid lubrication film increased. Especially when the content of MoS<sub>2</sub> was 3%, the electrical conductivity and the mechanical properties showed a better balance between themselves, and wear performance of the composite materials are the best.

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